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LLNL-CONF-402391

Structure and Phase Transformations in Pu Alloys

A. J. Schwartz, T. B. Massalski, H. Cynn, W. J. Evans, D. L. Farber, M. A. Wall, K. J. M. Blobaum, K. T. Moore, J. R. Jeffries

March 19, 2008

2008 MRS Spring Meeting
San Francisco, CA, United States
March 24, 2008 through March 28, 2008

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Structure and Phase Transformations in Pu Alloys

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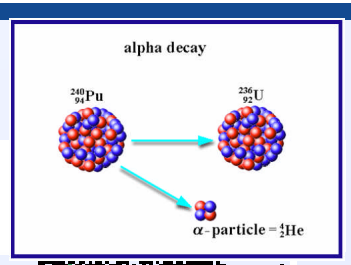
This work performed under the auspices of the U.S. Department of Energy by
Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

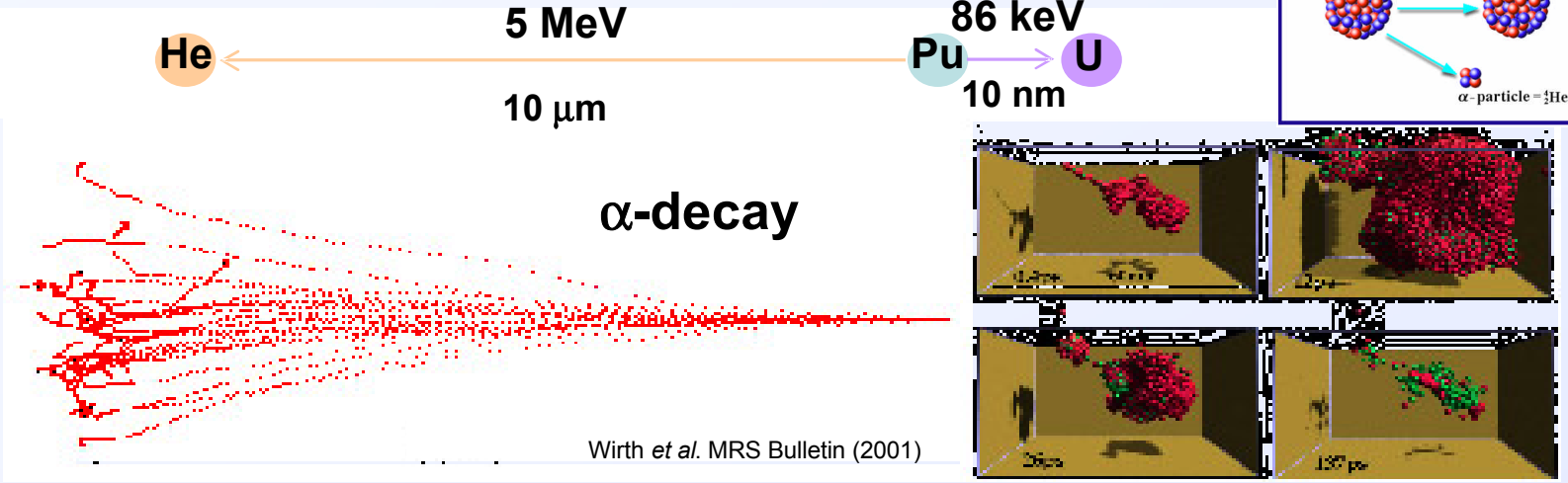
LLNL-CONF-xxxxxx

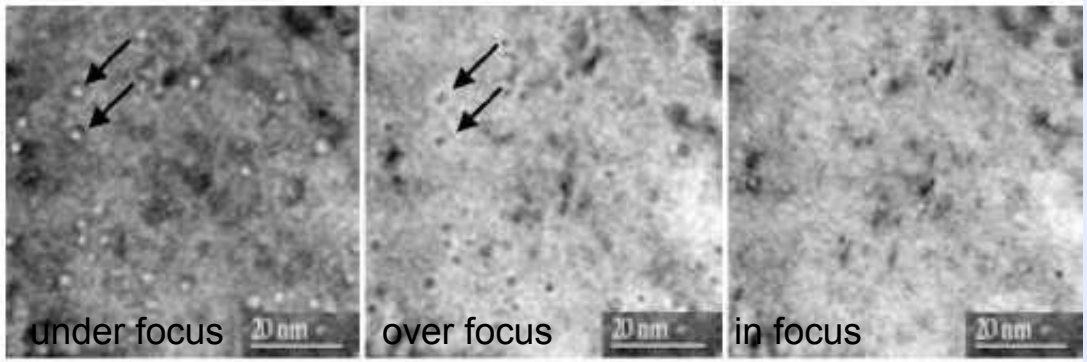
We shall focus in this review on the materials science aspects of Pu and Pu-based alloys

- **The usual connections are as follows:**
  - **Free energy and thermodynamics**
  - **Phase diagrams**
  - **Transformations (nucleation and growth)**
    - **Isothermal martensitic phase transformations**
    - **Pressure-induced phase transformations**
  - **Microstructure**
  - **Properties**

Self-irradiation damage is the primary source of microstructural change with age



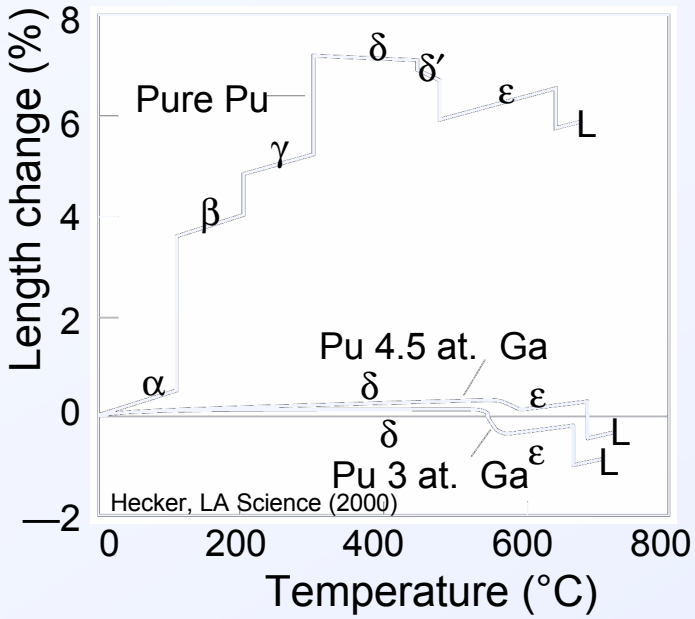




Schwartz et al. Phil Mag (2005)

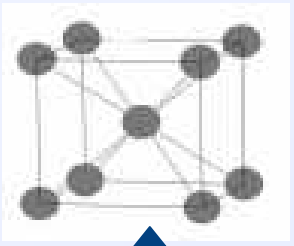
Through focus transmission electron microscopy images of a 42-year-old Pu-Ga alloy

Plutonium undergoes five solid-solid allotropic phase transformations between the ground state and the liquid



Liquid (640°C +)
ρ = 16.5 g/cm^3

ε (486°C - 640°C)
b.c. cubic ($Im\bar{3}m$)
ρ = 16.5 g/cm^3



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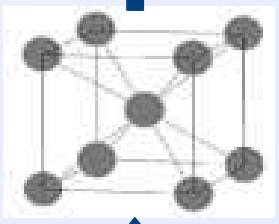
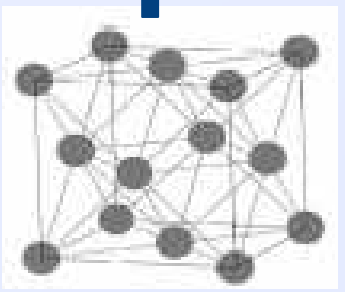
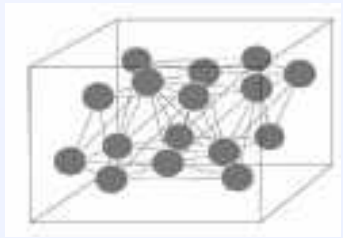


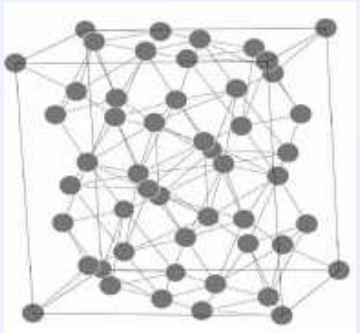
δ′ (468°C - 486°C)
b.c. tetragonal (I4/mmm)
ρ = 16.0 g/cm^3

–0.5%

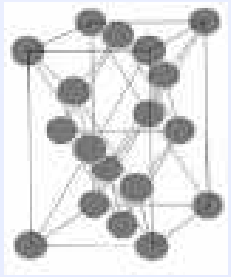




10%



3.5%



7%

α (Low temperature - 126°C)
monoclinic ($P2_1/m$)
ρ = 19.8 g/cm^3

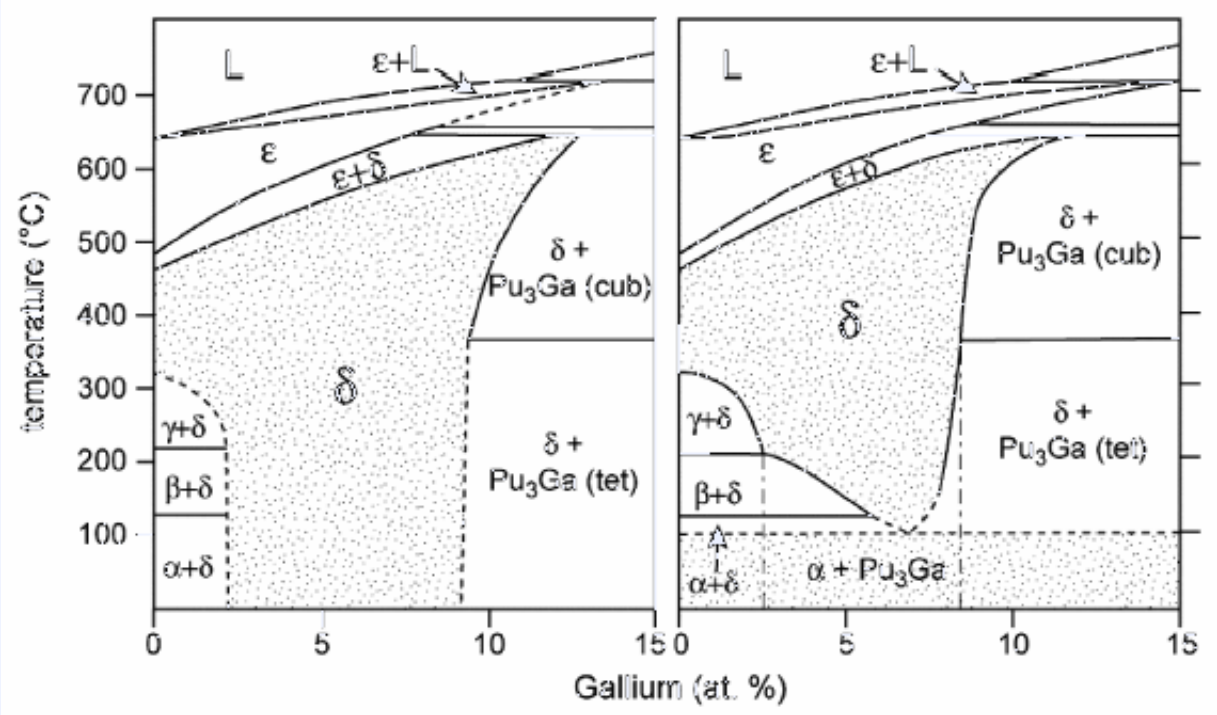
β (126°C - 214°C)
base.c. monoclinic (C2/m)
ρ = 17.8 g/cm^3

γ (214°C - 323°C)
f.c. orthorhombic (Fddd)
ρ = 17.1 g/cm^3

δ (323°C - 468°C)
f.c. cubic ($Fm\bar{3}m$)
ρ = 15.9 g/cm^3

For decades, the "West" accepted that the δ phase was thermodynamically stable at ambient conditions

US Diagram **Russian Diagram**



Ellinger, Land, and Struebing, J. Nuc. Mat. (1964)

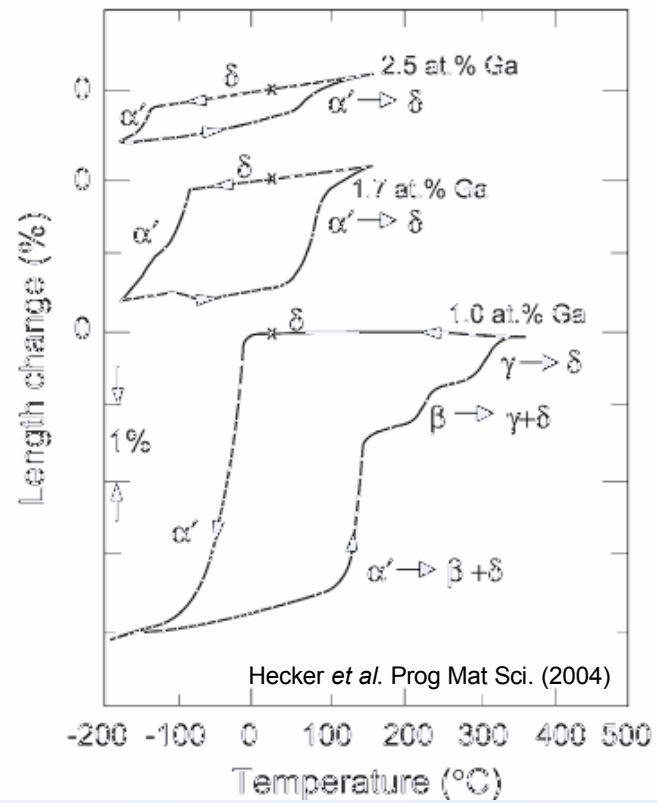
Hecker and Timofeeva, LA Science (2000)

The δ-phase retained to room temperature is metastable
Timofeeva (2003) estimated 10,000 years to decompose

Chebotarev, Plutonium and Other Actinides 1975 (1975)
Adler, Met Trans (1991)
Timofeeva, Aging Studies and Lifetime Extension of Materials (2003)

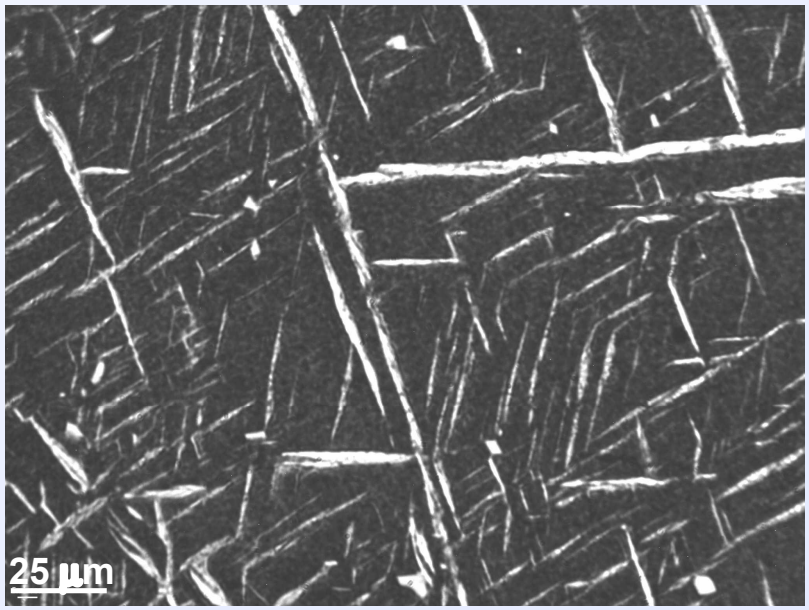
Upon cooling to sub-ambient temperatures, δ transforms to α′ via an isothermal martensitic transformation

The δ → α′ isothermal martensitic transformation can be induced with continuous cooling experiments



Hecker *et al.* Prog Mat Sci. (2004)

Pu - 2.0 at.% Ga
–155°C, 4 hours
Optical micrograph



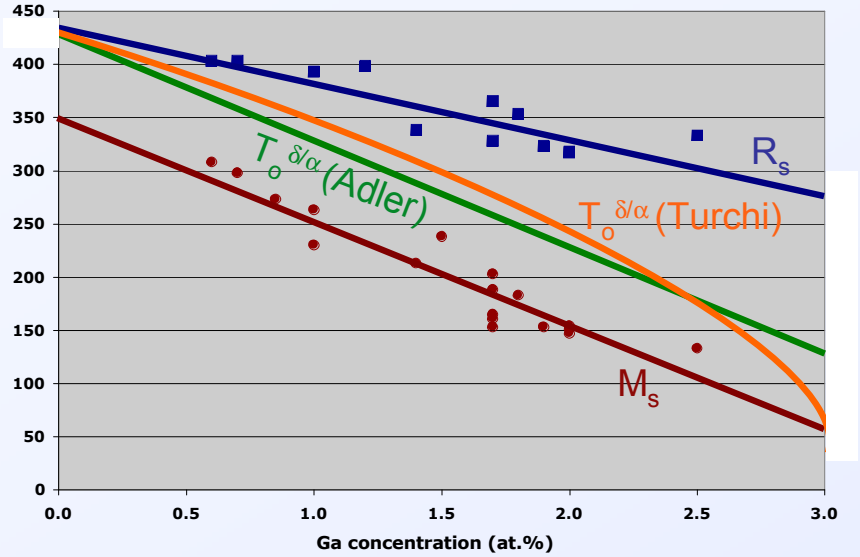
Wall *et al.* LLNL (2008)

Partially transformed (δ + α' phases)

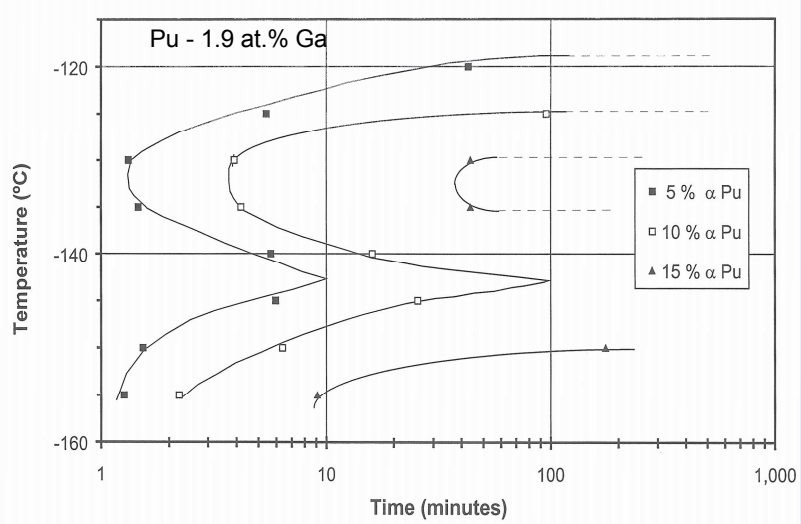
Like the δ-phase at room temperature, α′ is also metastable

The α′ particles that form from the isothermal martensitic transformation appear as lathes in optical microscopy

The martensite start temperature, M_s, and martensite reversion temperature, R_s, are a function of Ga content



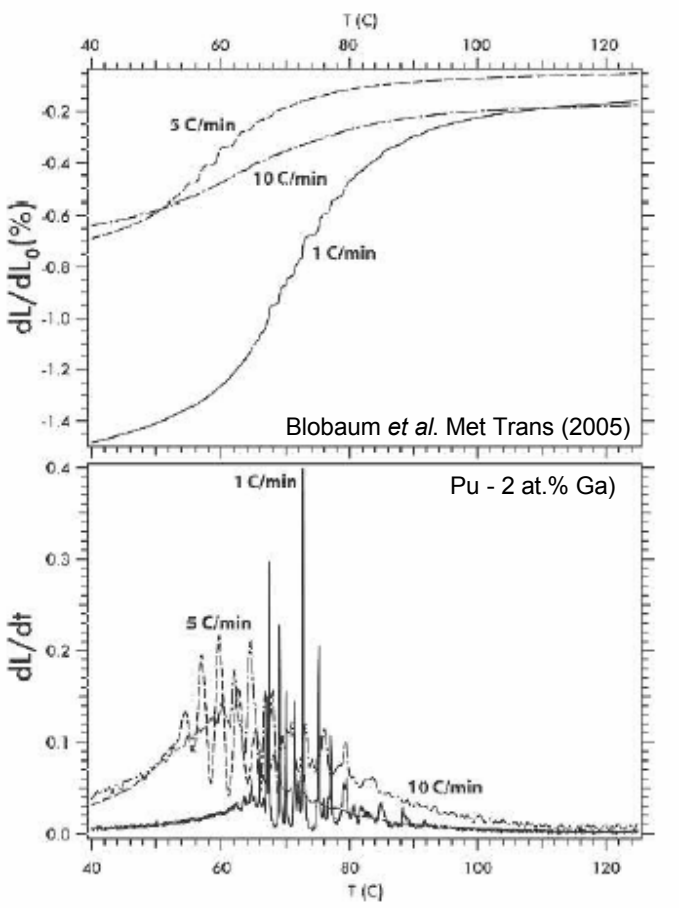
Double-C plots of a Pu - 1.9 at.% Ga alloy

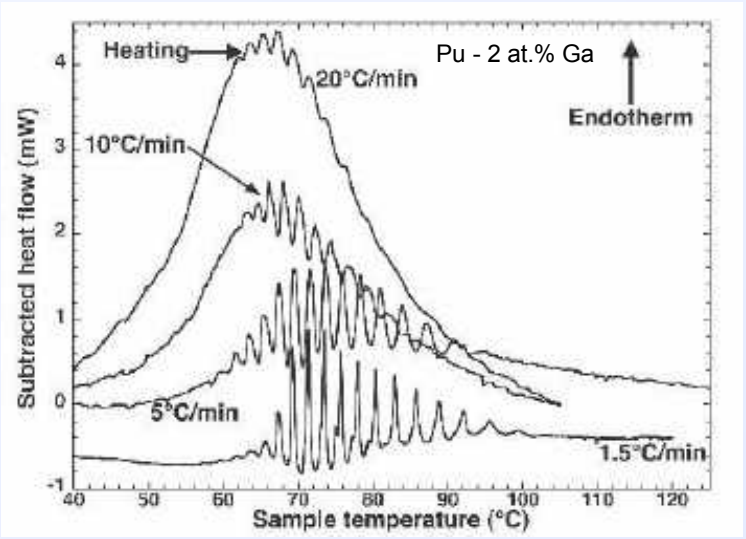


Orme *et al.* Pu & Other Actinides (1975)

The δ → α′ isothermal martensitic transformation goes to ~ 25% completion

α′ → δ reversion has been shown to be via a avalanche martensitic mode in both dilatometry and DSC





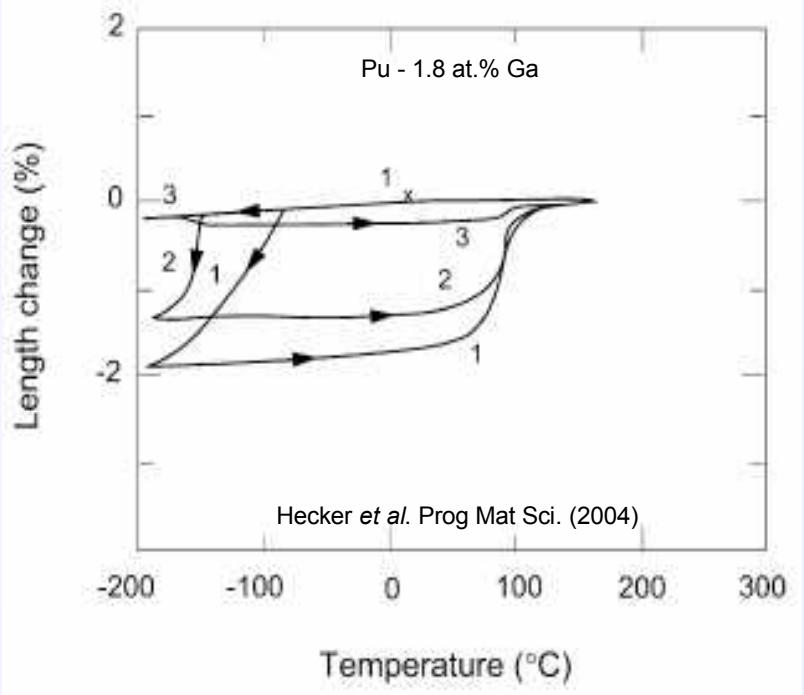
Blobaum *et al.* Met Trans (2005)

Differential scanning calorimetry of the α′ → δ reversion shows periodic spikes

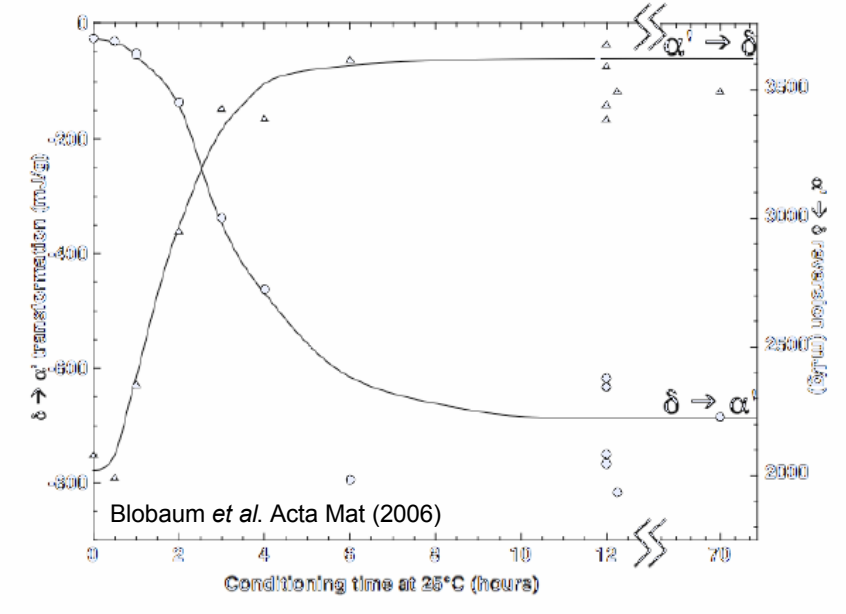
Dilatometry traces through the α′ → δ reversion exhibit steps

The derivative (dL/dt) reveals periodic spikes

The amount of the δ → α′ transformation is dependent on details of the thermal cycling and "conditioning"



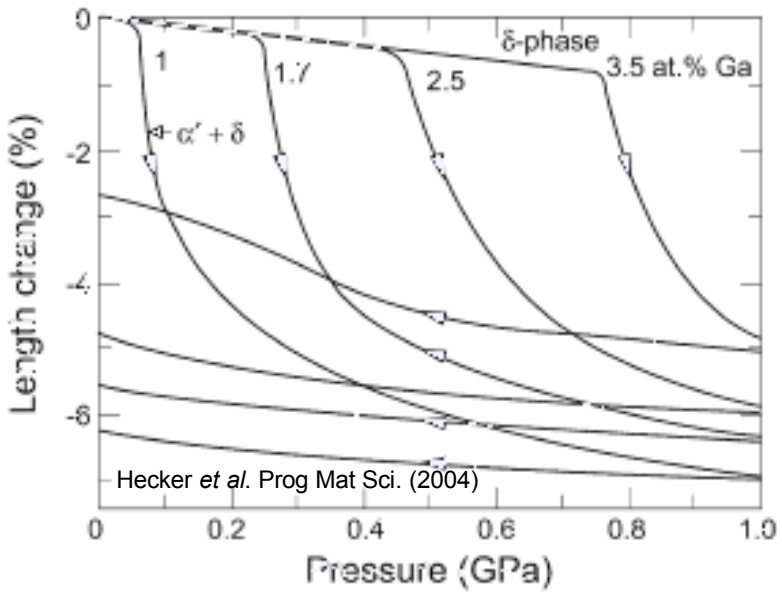
The amount of transformation in Pu - 1.8 and 2.0 at.% Ga alloys decrease with each thermal cycle



- Conditioning times of ~6 hours are required for reproducible amounts of transformation
- α_m embryos may be forming as a precursor to the δ → α + Pu_3Ga
- These α_m embryos initiate α′ on subsequent cooling

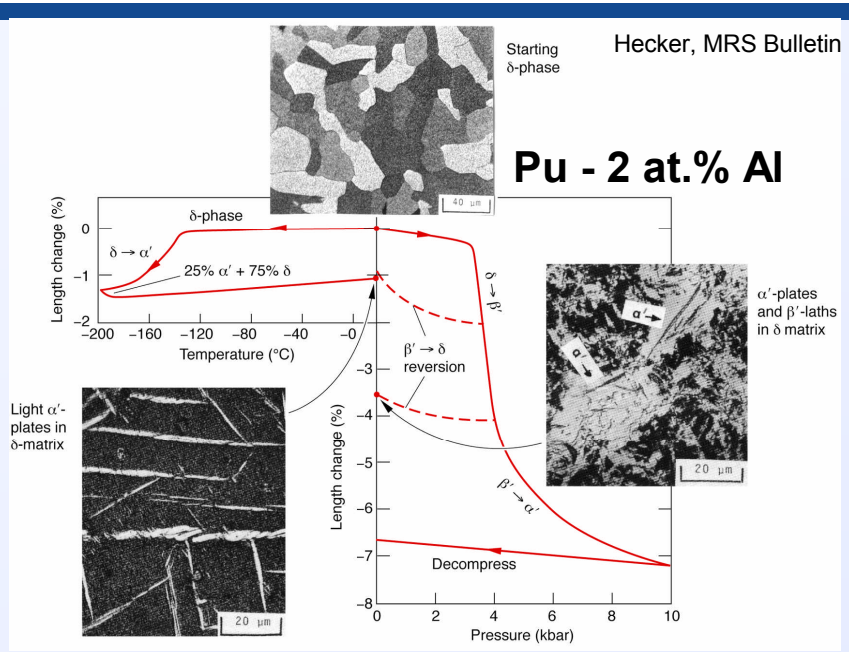
The δ → α′ transformation can also be induced by pressure

Pu - 2 at.% Ga



- Under pressure, Pu - Ga alloys transform directly to α′ and undergo either a direct (α′ → δ) or indirect (α′ → β′ + δ → γ′ + δ → δ) reversion
- Reversion characteristics are similar to those in thermally-induced transformations

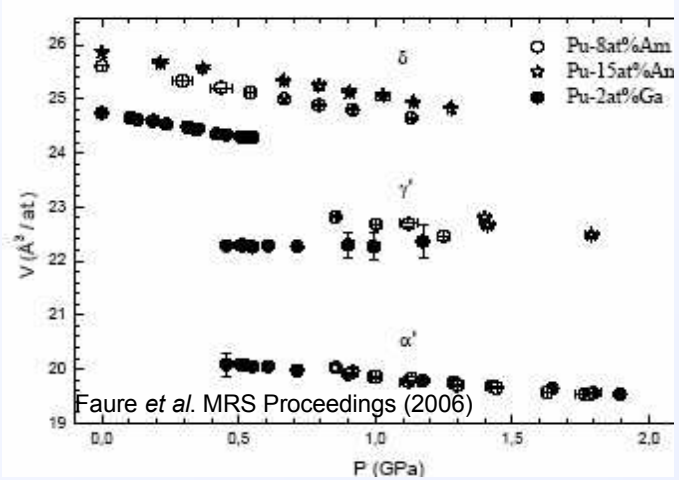
Pu - 2 at.% Al



Pu - 2 at.% Al alloys transform first to β′ then to α′ under pressure

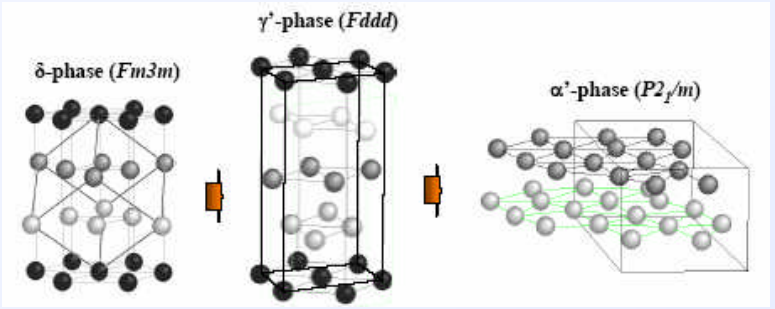
Why do Pu-Al alloys transform through β′ whereas Pu-Ga alloys transform directly to α′?

Diamond anvil cell experiments on a Pu - 2 at.% Ga alloy reveal δ → γ′ → α′ transformation sequence

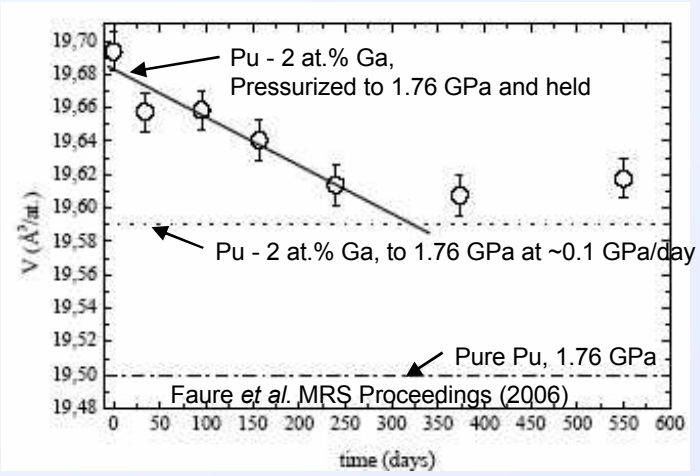


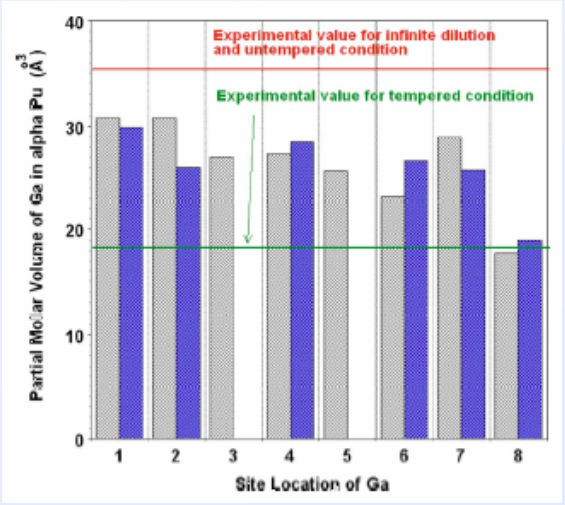
Faure *et al.* MRS Proceedings (2006)

Faure *et al.* MRS Proceedings (2006)



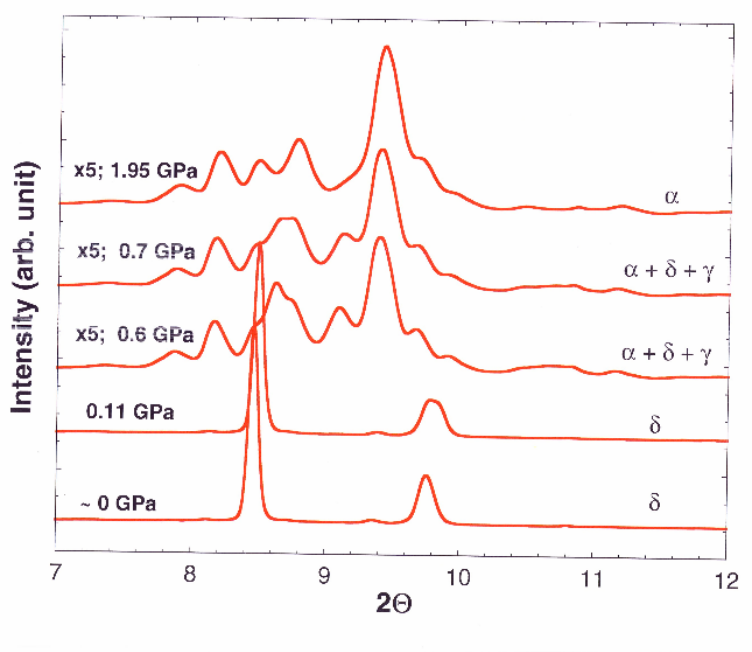
In the DAC, Pu - 2 at. Ga transforms through the sequence δ → γ′ → α′

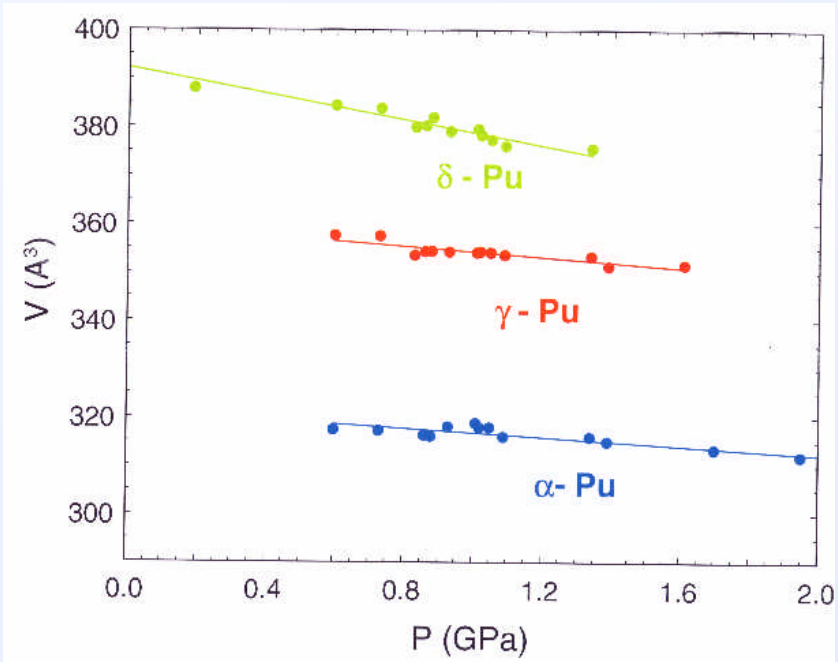




Sadigh and Wolfer, PRB (2005)

Recent experiments at LLNL also suggest intermediate transitions between δ and α′



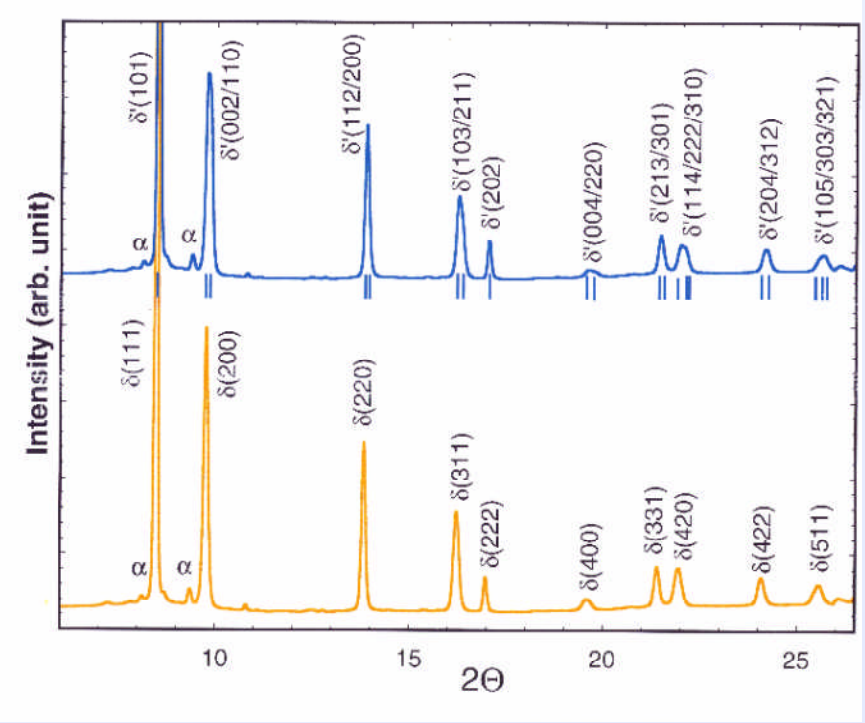


- Diffraction peaks of the δ phase split at low pressures to a γ like structure
- γ like structure structure appears at ~0.6 Gpa

- γ like structure structure disappears at ~1.6 Gpa

At low pressure, δ phase distorts to δ′

- Small amounts (<~1%) of γ′ and α′ coexist with δ at ambient
- Is identified at ~0.1 GPA
  - I4/mmm (S.G. 139, z = 2)
  - a = 3.240Å
  - c = 4.617Å
  - V = 48.47Å3 (0.2% denser than δ -Pu
  - Pressure induces growth of γ′ and α′



Upon cooling, Harbur reported that a 0.68 at.% Ga alloy has a density intermediate between δ and α phases

Harbur, JALCOM (2007)

QuickTime™ and a
compressed) decompressor
eded to see this picture.

After compressing to 1 GPa

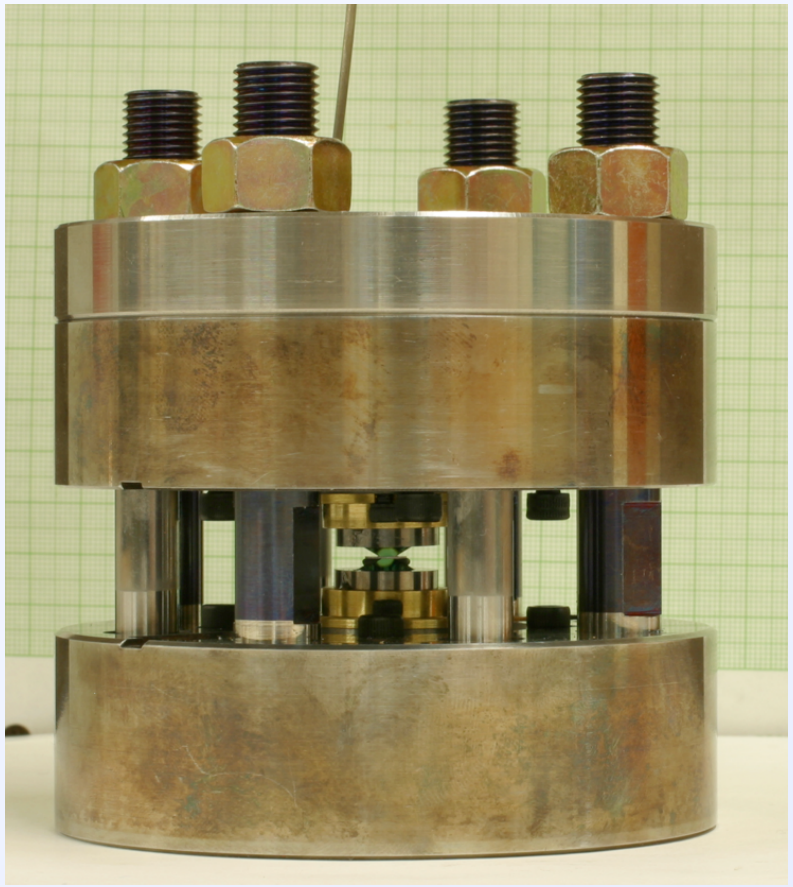
Alloy	% α'	% δ	% amorphous
1.0 at.% Ga	87	0	13
1.7 at.% Ga	66	0	34
2.5 at.% Ga	68	12	20

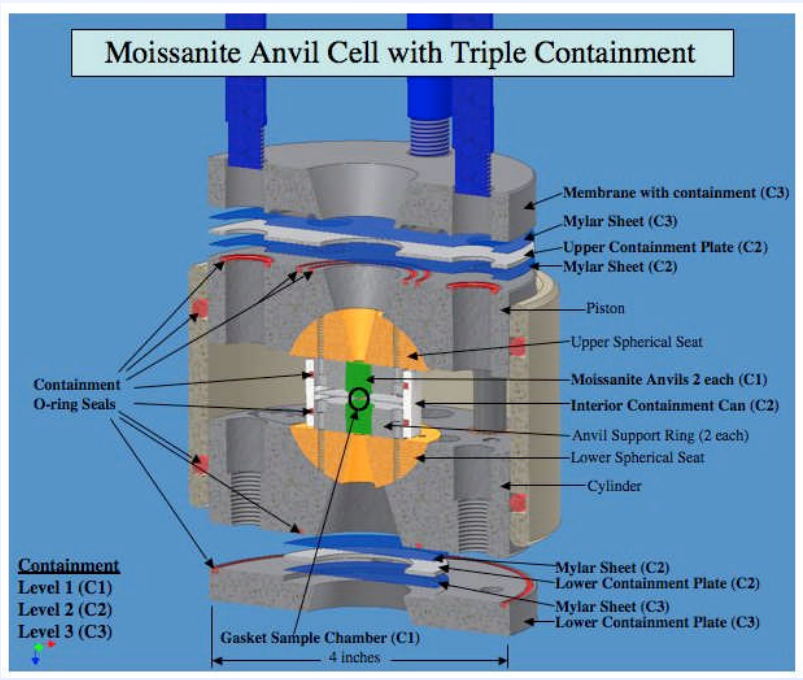
Harbur, JALCOM (2007)

Harbur proposes that the δ phase transforms to α' + amorphous phase

- **on cooling low solute alloys**
- **under pressure**

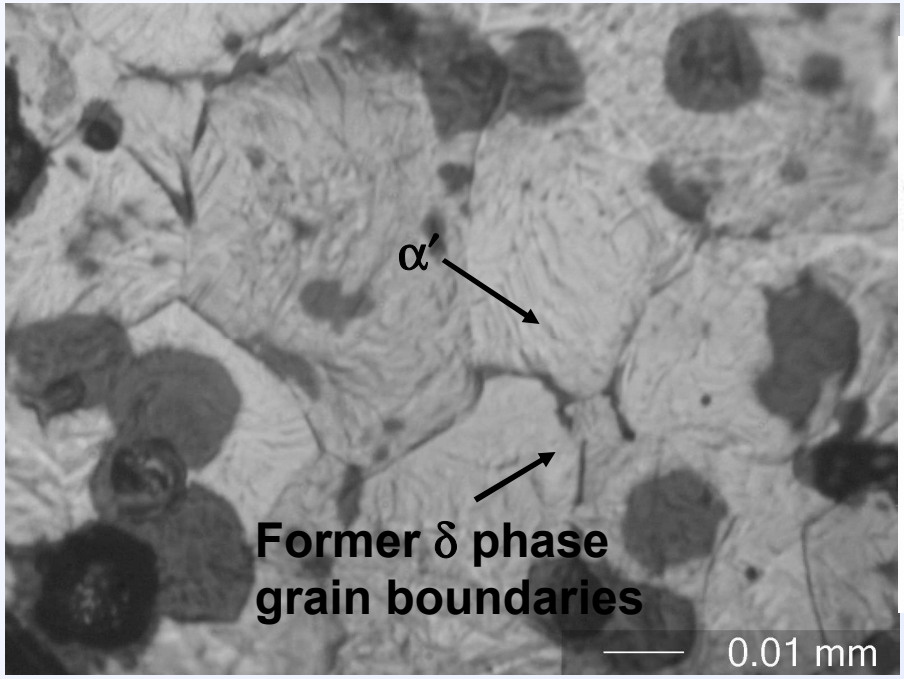
We are coupling low pressure recovery experiments with TEM to elucidate the mechanism and morphology

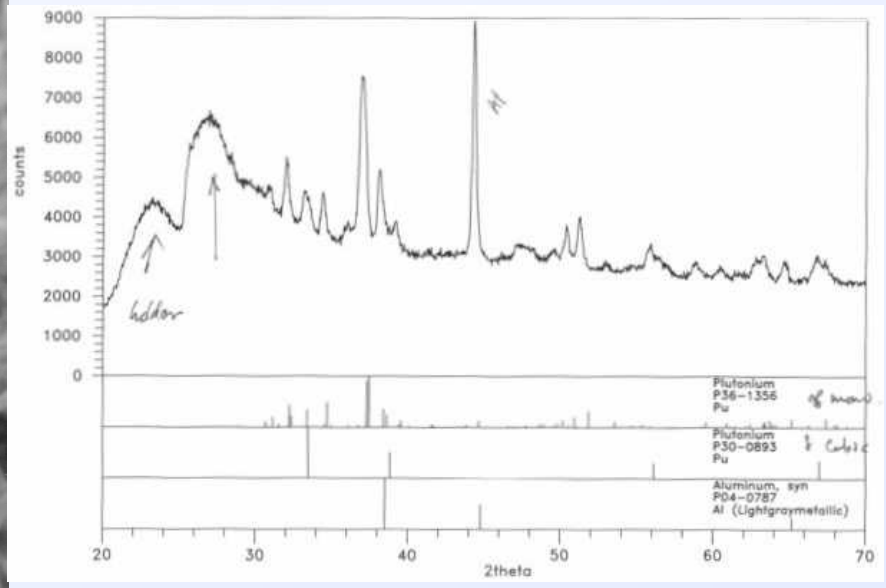




2.3 mm diameter specimens are slowly compressed to 1 GPa in the large volume moissanite anvil cell

Optical microscopy and x-ray diffraction of the compressed specimen reveals α′ and δ phases

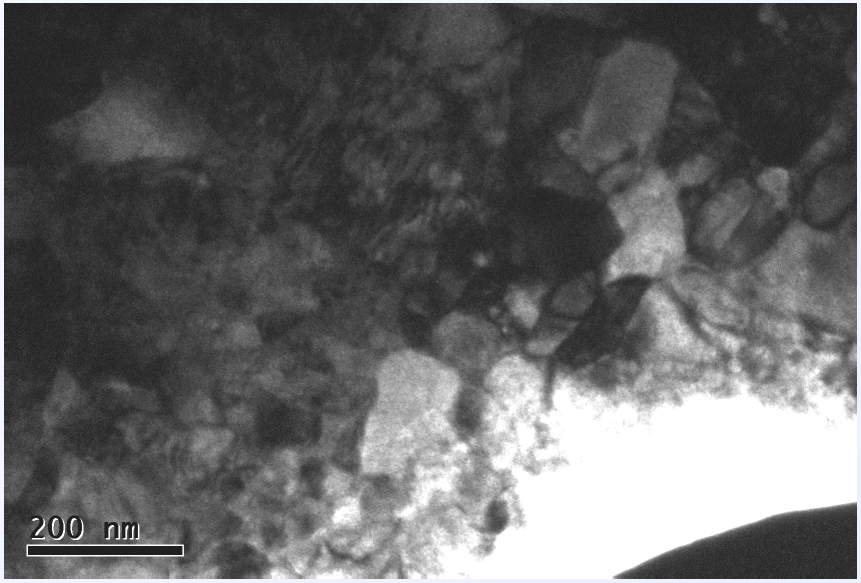


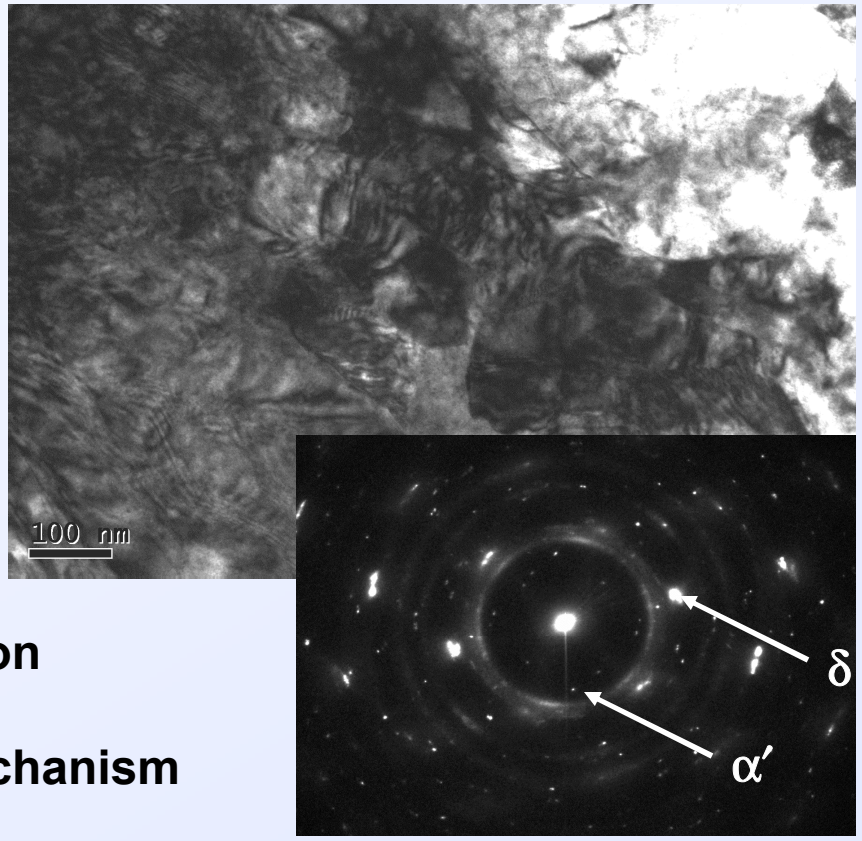


Optical microscopy does not have the resolution to differentiate between phases

Our X-ray diffraction does not indicate the presence of an amorphous phase

Preliminary TEM reveals fine-grained α′ and small amounts of δ – no evidence of an amorphous phase



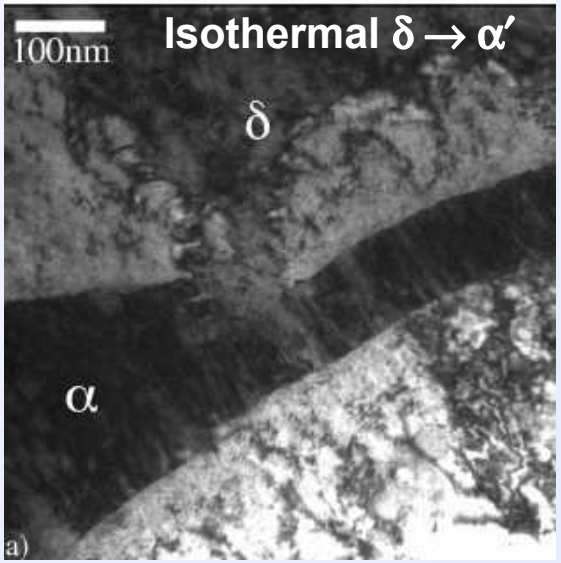


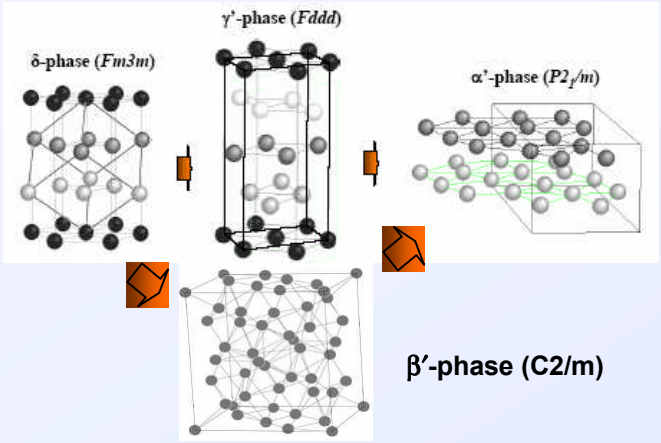
Pressure-induced δ → α′ transformation
- **Average α′ grain size ~ 100s nm**
- **Implies nucleation dominated mechanism**

δ phase is observed dispersed between the α′ grains
- **High dislocation density**
- **No apparent orientation relationship (yet)**

Summary

- **Low temperature isothermal δ → α′ transformation**
  - Nucleation and growth are limited
  - Large lath-shaped particles form
  - Intermediate phases are possible
- **Pressure-induced δ → α′ transformation**
  - Nucleation dominates
  - Very fine grain size results
  - No evidence of the amorphous phase
  - Intermediate phases exist





β′-phase (C2/m)